

EFFECTS OF GROUNDWATER CHEMICAL COMPOSITIONS IN DEEP SALINE AQUIFERS ON CO₂ GEOLOGICAL SEQUESTRATION

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ABSTRACT

Groundwater chemical composition exerts a strong effect on the dissolution of carbon dioxide, in turn affecting the evaluation and prediction of carbon dioxide (CO₂) geological sequestration (CGS). Based on Duan's CO₂ solubility model (2003, 2006), which considered the effects of ions, this paper analyzes the effects of five factors: (1) the equivalent mole fraction of (Na⁺+K⁺) in cations, (2) the equivalent mole fraction of Cl⁻ in anions, (3) salinity, (4) pressures and (5) temperatures on CO₂ solubility. We then incorporate this model into TOUGH2/ECO2N code as an option for CO₂ solubility calculation. We conclude by considering two typical problems, radial flow from a CO₂ injection well and convective mixing, to study the effects of groundwater chemical compositions on CGS. The results indicate that under different temperatures, pressures, and salinity, the dissolved CO₂ increases with the increase in equivalent mole fraction of (Na⁺+K⁺) compared to (Ca²⁺+Mg²⁺) and decreases with the increase in equivalent mole fraction of Cl⁻ compared to SO₄²⁻. Low temperatures, high pressures, and low salinity contribute to an increase in the dissolved CO₂. The difference in dissolved CO₂ between cations in low salinity and anions in high salinity become small. Simulations of the two typical problems showed that groundwater chemical compositions have a significant effect on dissolved CO₂ in the two-phase region, but this effect is not obvious on the distribution of pressure and saturation, owing to the scale of the problem. The NaCl groundwater benefited from convective mixing and enhanced solubility trapping more than CaCl₂.

1. INTRODUCTION

In recent years, the recognition of climate change as a major global problem has increased. Several special reports from the Intergovernmental Panel on Climate Change (IPCC) suggest that the large emissions of greenhouse gases is one of the main factors in climate change, especially emissions of CO₂ (IPCC, 2005; IPCC, 2007). Researchers around the world now generally hold the view that reducing the emissions of greenhouse gas is very important for the mitigation of global climate change. Given the large amounts of groundwater with high total dissolved solids (TDS) (often >10,000mg/L), which cannot be used as sources of drinking water, and enough porous space, deep saline aquifers are being considered as possible sites for long-term, high-volume CO₂ storage..

Injecting supercritical CO₂ (called "gas" here for simplicity) into a deep saline aquifer will induce a series of complicated physical and chemical processes, including multiphase fluid and heat flow, water-rock reactions, geomechanical changes, and so on. The methods for knowing these processes primarily come down to experiments and numerical simulations. Numerical simulation, a relatively low-cost method for studying complex geological conditions within deep formations, is widely used to study CGS in deep saline aquifers. The TOUGH family of codes has often been used for this purpose (e.g., Pruess and Garc a, 2002; Pruess, 2003; Xu et al., 2004).

Injecting CO₂ into saline aquifers displaces the formation water and results in an increase in pressure. Some CO₂ dissolves in formation water as solubility trapping. The acidity of the formation water increases because of the dissolved CO₂ and enhances water-rock interaction, which transforms

CO₂ into carbonate minerals as mineral trapping. The difference in density between CO₂ and water drives the upward migration of CO₂ and large amounts of CO₂ accumulate beneath the low permeability rocks as hydrodynamic trapping. These coupled processes are affected by the geological and hydrogeological conditions, structure, temperature, pressure and so on, which makes the migration and transformation of CO₂ extremely complex. Accurate prediction of these processes thus requires a model that can reliably track and account for this complexity.

For various evaluations and predictions regarding CGS in deep saline formations, CO₂ dissolution is an important process, one which directly affects late mineral trapping and feeds back to early hydrodynamic trapping. The calculation of CO₂ solubility in TOUGH2/ECO2N is similar to (but not the same as) Spycher's mutual solubilities model, based on the equilibrium between gas and aqueous phases, and considers the effect of salinity (Spycher, et al., 2003; Spycher and Pruess 2005; Pruess, 2005). Although the groundwater chemical components of deep formations are mainly dominated by the ions of Na⁺ and Cl⁻, they also contain other ions such as Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻. Therefore, the method in TOUGH2 ECO2N module that only considers the effect of Na⁺ and Cl⁻ on CO₂ solubility is not broad enough. Based on Duan's CO₂ solubility model (Duan et al., 1992; Duan and Sun, 2003; Duan and Sun 2006) which considers different ionic effects, this paper incorporated Duan's model into the ECO2N module as an option for CO₂ solubility calculation, and then, using this modified code, analyzed the effects of groundwater chemical components on CGS in deep saline aquifers.

2. GOVERNING EQUATIONS AND NUMERICAL PROCEDURE

2.1. Mass and Energy Balance Equations

Based on mass and energy conservation, the characterization for CO₂-water-salt system can be expressed as (Pruess et al., 1999):

$$\frac{d}{dt} \int_{V_n} M^\kappa dV = \int_{\Gamma_n} \mathbf{F}^\kappa \cdot \mathbf{n} d\Gamma + \int_{V_n} q^\kappa dV \quad (1)$$

The left accumulation term of mass and energy is given by (Pruess et al., 1999):

$$M^\kappa = \sum_{\beta=A,G} \phi S_\beta \rho_\beta X_\beta^\kappa, \quad \kappa = w, i, g \quad (2)$$

$$M^{\kappa+1} = (1 - \phi) \rho_R C_R T + \sum_{\beta=A,G} \phi S_\beta \rho_\beta u_\beta \quad (3)$$

The right flux term of mass and energy follows Darcy's law and Fick's law such as (Pruess et al., 1999):

$$\mathbf{F}_\beta^\kappa = -k \frac{k_{r\beta} \rho_A}{\mu_\beta} X_\beta^\kappa (\nabla P_\beta - \rho_\beta \mathbf{g}) + \mathbf{J}_\beta^\kappa, \quad \kappa = w, i, g \quad (4)$$

$$\mathbf{F}_\beta^{\kappa+1} = -\lambda \nabla T + \sum_\beta h_\beta \mathbf{F}_\beta \quad (5)$$

where M is mass or energy accumulation; \mathbf{F} is flux of mass or energy; V is volume; Γ and \mathbf{n} are surface and normal vector; $\kappa = w, i, g$ are water, salt, and gas, respectively; $\kappa + 1$ is energy; ϕ is porosity; S is saturation; ρ is density; X is mass fraction; u is internal energy; C is specific heat; k and k_r are, respectively, permeability and relative permeability; P is pressure; T and t are temperature and time, respectively; \mathbf{J} is the diffusion term; λ is thermal conductivity; h is specific enthalpy; and q is sink/source.

2.2. Space and Time Discretization

The discretization in space uses the integral finite difference (IFD) method. The discretization in time is implicit. Equation (1) can be discretized as (Pruess et al., 1999):

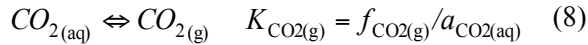
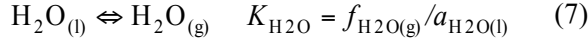
$$R_n^{\kappa,k+1} = M_n^{\kappa,k+1} - M_n^{\kappa,k} - \frac{\Delta t}{V_n} \left\{ \sum_m A_{nm} F_{nm}^{\kappa,k+1} + V_n q_{nm}^{\kappa,k+1} \right\} = 0 \quad (6)$$

where R and A are residuals and area, respectively. The nonlinearity of Equation (6) results in difficulty to be solved directly. Therefore, the Newton-Rapson iteration is employed. Jacobian matrixes are evaluated by numerical differentiation. The linear equations are solved by sparse direct matrix methods or iteratively by means of preconditioned conjugate gradients.

3. MUTUAL SOLUBILITIES MODEL OF CO₂ AND GROUNDWATER

3.1. TOUGH2/ECO2N's Mutual Solubilities Model

TOUGH2/ECO2N is based on Spycher's mutual solubilities model, which in turn is based on equilibrium between the aqueous and gas phases (Spycher, et al., 2003):



Considering the effect of pressure and temperature on equilibrium constants, the mole fraction of gas and water in the different phases can be calculated as (Spycher, et al., 2003):

$$y_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^0 (1 - x_{\text{CO}_2})}{\phi_{\text{H}_2\text{O}} P_{\text{tot}}} \exp\left(\frac{(P - P^0) \bar{V}_{\text{H}_2\text{O}}}{RT}\right) \quad (9)$$

$$x_{\text{CO}_2} = \frac{\phi_{\text{CO}_2} (1 - y_{\text{H}_2\text{O}}) P_{\text{tot}}}{55.508 K_{\text{CO}_2(g)}^0} \exp\left(-\frac{(P - P^0) \bar{V}_{\text{CO}_2}}{RT}\right) \quad (10)$$

where K , f , and a are equilibrium constants, fugacities of the gas components, and the activity of components in the aqueous phase, respectively. $y_{\text{H}_2\text{O}}$ and x_{CO_2} are H_2O mole fraction in the gas and CO_2 mole fraction in the aqueous phase, respectively; ϕ is the fugacity coefficient. P_{tot} and P are total pressure and partial pressure. R is the gas constant, and T is temperature. The above model is extended to take into account the effect of salinity (including monovalent and divalent cations, Cl^- and SO_4^{2-}) by using activity coefficients (on a mole fraction scale) (Spycher and Pruess, 2005). However, in TOUGH2/ECO2N for CO_2 solubility calculation there exists some difference from Spycher's model because TOUGH2/ECO2N doesn't use the same equation of state for PVT property and only considers the effect of Na^+ and Cl^- .

3.2. Duan's CO₂ Solubility Model

The chemical potential of CO_2 in both the gas and liquid phase can be expressed, respectively, as (Duan and Sun, 2003):

$$\mu_{\text{CO}_2}^v(T, P, y) = \mu_{\text{CO}_2}^{v(0)}(T) + RT \ln(y_{\text{CO}_2} P) + RT \ln \varphi_{\text{CO}_2}(T, P, y) \quad (11)$$

$$\mu_{\text{CO}_2}^l(T, P, m) = \mu_{\text{CO}_2}^{l(0)}(T, P) + RT \ln m_{\text{CO}_2} + RT \ln \gamma_{\text{CO}_2}(T, P, m) \quad (12)$$

At equilibrium, $\mu_{\text{CO}_2}^v = \mu_{\text{CO}_2}^l$. According to these equations and applying a Pitzer-type model for calculating the activity of CO_2 in the liquid phase, the CO_2 solubility in aqueous solutions can be derived as follows (Duan and Sun, 2003):

$$\ln m_{\text{CO}_2} = \ln(y_{\text{CO}_2} P) - \frac{u_{\text{CO}_2}^{l(0)}}{RT} + \ln \varphi_{\text{CO}_2} - \sum_c 2\lambda_{\text{CO}_2-c} m_c - \sum_a 2\lambda_{\text{CO}_2-a} m_a - \sum_c \sum_a \zeta_{\text{CO}_2-c-a} m_c m_a \quad (13)$$

For certain groundwater components, CO_2 solubility can be expressed as (Duan and Sun, 2003):

$$\ln m_{\text{CO}_2} = \ln(y_{\text{CO}_2} P) - \frac{u_{\text{CO}_2}^{l(0)}}{RT} + \ln \varphi_{\text{CO}_2} - 2\lambda_{\text{CO}_2-\text{Na}}(m_{\text{Na}} + m_{\text{k}} + 2m_{\text{ca}} + 2m_{\text{Mg}}) - \zeta_{\text{CO}_2-\text{Na}-\text{Cl}} m_{\text{Cl}}(m_{\text{Na}} + m_{\text{k}} + m_{\text{ca}} + m_{\text{Mg}}) + 0.07m_{\text{SO}_4} \quad (14)$$

The mole fraction of water in the gas phase is (Duan and Sun, 2003):

$$y_{\text{CO}_2} = (P - P_{\text{H}_2\text{O}}) / P \quad (15)$$

where $\mu_{\text{CO}_2}^v$ and $\mu_{\text{CO}_2}^l$ are the chemical potential of CO_2 in the gas and liquid phases, respectively; $\mu_{\text{CO}_2}^{v(0)}$ and $\mu_{\text{CO}_2}^{l(0)}$ are chemical potentials of vapor and liquid CO_2 , respectively; and y_{CO_2} and m_{CO_2} are mole fractions of CO_2 in the gas phase and molality of CO_2 in the liquid phase, respectively. φ and γ are fugacity and activity coefficients, respectively; P is total pressure and $P_{\text{H}_2\text{O}}$ is the vapor pressure of pure H_2O ; λ and ζ are Pitzer parameters, and m denotes the molality of the ion.

4. ANALYSIS OF CO₂ SOLUBILITY FOR DIFFERENT GROUNDWATER CHEMICAL COMPOSITIONS

The groundwater chemical components in deep saline aquifers are dominated by sodium chloride. However, in carbonate formations, the long-term dissolved carbonate minerals induce an increase of Ca^{2+} in groundwater, which typically makes the

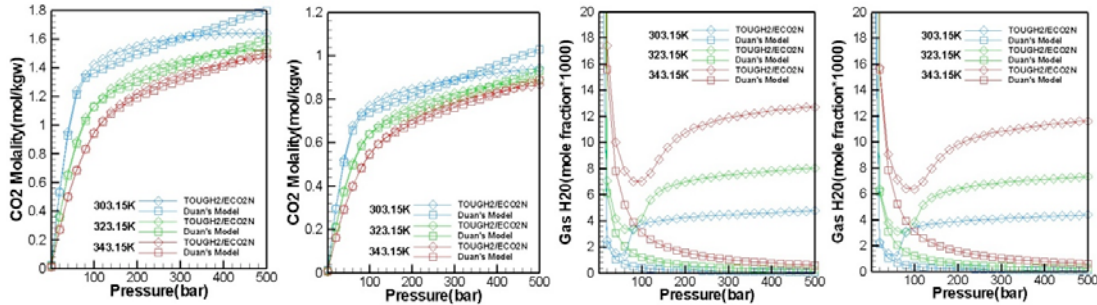
water become of the Ca-Na-Cl type. Also, it contains some SO_4^{2-} due to dissolution of gypsum. Consequently, this paper uses two types of water, Na-Cl type and Ca-Na-Cl type, containing some SO_4^{2-} , to analyze the effects of different ions on the solubility of CO_2 .

The effects that ions with the same charges (i.e. Na^+ and K^+) have on the solubility of CO_2 are difficult to evaluate. With this in mind, we consider the five factors to study such effects: the equivalent mole fraction of $(\text{Na}^+ + \text{K}^+)$ in cations, the equivalent mole fraction of Cl^- in anions, salinity, pressures and temperatures.

Differences between the original ECO2N's and Duan's models are evaluated at two sodium chloride concentrations: 0.0 M (molality) and 3.0 M. The results show that the difference in CO_2 solubility between the two models can be neglected when the temperature is high, but there is a difference when temperature is low (See Figure 1a and 1b). However, the prediction of mole fraction of H_2O in the gas phase shows

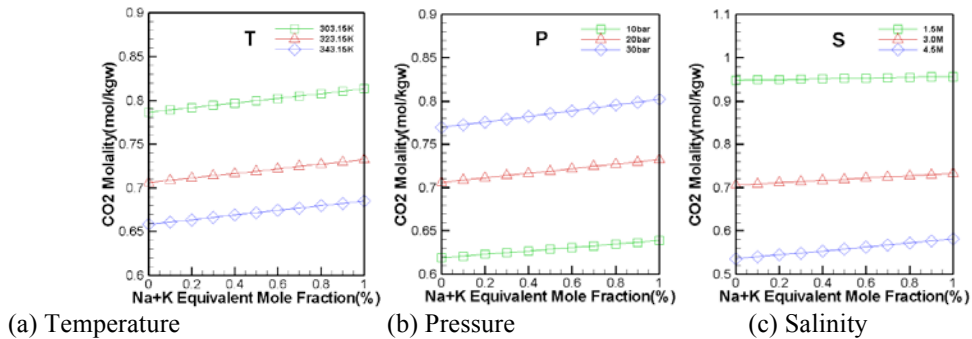
significant differences (see Figure 1c and 1d) because Duan's model does not account for salt and other non-ideal mixing effects in the partitioning of water into CO_2 .

Figure 2 and Figure 3 show that under the different temperatures, pressures, and salinity the dissolved CO_2 increases with the increase in equivalent mole fraction of $(\text{Na}^+ + \text{K}^+)$ compared to $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and decreases with the increase in equivalent mole fraction of Cl^- compared to SO_4^{2-} . Low temperatures, high pressures, and low salinity contribute to an increase in the dissolved CO_2 . However, the difference in dissolved CO_2 between cations in the low salinity and that between anions in the high salinity become small. (See Figure 2c and Figure 3c). The effects of Cl^- in the high salinity is different from that in the low salinity, with a slight increase as the equivalent mole fraction of Cl^- increases (See Figure 3c).



(a) CO_2 molality(0M NaCl) (b) CO_2 molality(3M NaCl) (c) H_2O mass fraction in the gas phase(0M) (d) H_2O mass fraction in the gas phase(3M)

Figure 1. Comparing Duan's model to the original ECO2N's model on CO_2 - H_2O mutual solubility



(a) Temperature (b) Pressure (c) Salinity

Figure 2. Effects of temperature, pressure and salinity at different Na^+ equivalent mole fraction on CO_2 solubility (Note that $\text{Na} + \text{K}$ equivalent mole fraction is: $\frac{m(\text{Na} + \text{K})}{m(\text{Na} + \text{K}) + 2m(\text{Ca} + \text{Mg})}$, (a) is at the pressure of 200bar and salinity of 1.5M (b) is at the temperature of 323.15K and salinity of 1.5M (c) is at the pressure of 200bar and temperature of 323.15K)

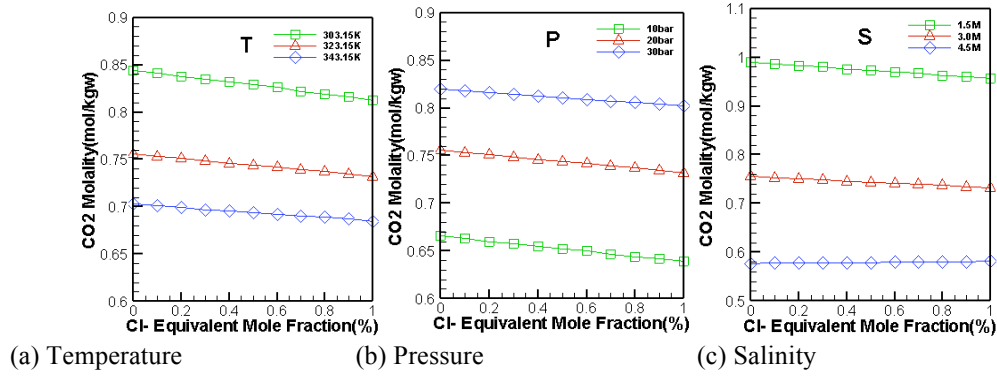


Figure 3. Effects of temperature, pressure and salinity at different Cl^- equivalent mole fraction on CO_2 solubility (Note that Cl^- equivalent mole fraction is: $\frac{m(\text{Cl})}{m(\text{Cl}) + 2m\text{SO}_4}$ (a),(b) and (c) are at the same conditions as Figure 2)

5. EFFECTS OF GROUNDWATER CHEMICAL COMPOSITIONS ON CGS

The effects of groundwater components are first demonstrated by solubility trapping. Two simple problems, including radial flow from a CO_2 injection well and convective mixing, are employed to investigate these effects.

5.1. Problem 1: Radial Flow from a CO_2 injection Well

The model used in this paper is similar to that of Pruess (Pruess, 2003), with a 100 m domain thickness aquifers at a depth of 1.2 km. Radial length is extended to the greater distance of 100 km. The number of gridblocks is 6000, with 1000 gridblocks for the first 1 km and 5000 gridblocks further away. The upper and lower boundaries of this model are assumed to be impermeable cap rock and bedrock, respectively, and the lateral boundary is constant. Table 1 lists the setup of groundwater components for this model. A CO_2 injection well fully penetrates the aquifer, under conditions of 120 bar pressure, 45°C temperature, and a salinity of 15% by weight. CO_2 is injected at a constant rate of 50 kg/s. The fluid flow is run for a period of 10,000 days (27.38 years).

Table 1. Setup for formation water chemical components (mol/kgw)

Case NO.	$\text{Na}^+ + \text{K}^+$	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Cl^-	SO_4^{2-}
Base1	3.0	0.0	3.0	0.0
1	1.0	1.0	3.0	0.0
2	0.0	1.5	3.0	0.0
3	3.0	0.0	2.6	0.2

Note :because there is little CO_3^{2-} and HCO_3^- , this paper neglects them for this model.

Figures 4a, 4b, 5a, and 5b show that the impact of aqueous components on pressure and gas saturation is minimal. This is because the small differences in CO_2 solubility due to aqueous components at the large-field scale do not affect the time evolution and spatial distributions of pressure and gas saturation. However, the amount of dissolved CO_2 in the aqueous phase is affected by the aqueous components (See Figure 4c and 5c). It's obvious that $\text{Na}^+ + \text{K}^+$, SO_4^{2-} under this condition, are more helpful than $\text{Ca}^{2+} + \text{Mg}^{2+}$ and Cl^- for solubility trapping, respectively. We also see that there is some difference between the TOUGH2 original ECO2N's and Duan's CO_2 solubility models.

5.2. Problem 2: Convective Mixing

When CO_2 is injected into a saline formation, most of the CO_2 accumulates beneath the impermeable cap rock. In the two-phase region, the density of the aqueous phase increases due to the dissolved CO_2 , which can result in gravitational instability. The aqueous phase saturated with CO_2 will then migrate downward due to gravity, accompanied by an upward movement

of unsaturated water, giving rise to “convective mixing.” A three-dimensional high-resolution model is used to study this phenomenon (Zhang et al., 2007). The density-driven convection can increase the transformation rate of CO_2 from gas phase to the other phase and is favored as the long-term fate of the gas in saline aquifers. Zhang et al. (2007, 2011) have investigated the effects of convective mixing on long-term CO_2 geological storage, considering brine salinity, initial CO_2 gas saturation, the molecular diffusivity of dissolved CO_2 , mineralogical compositions, and geochemical reactions. We use the same 2-D model as Zhang et al. (2011) with 50 m height and 50 m width, to study the effects of water composition on convective mixing. The grids, initial and boundary condition are also the same as the study from Zhang et al. (2011). The other parameters are from Zhang et al. (2009). The water composition of the formation is the same as the Problem 1.

The density of aqueous with different components is calculated by converting to salt weight fraction for input into TOUGH2/ECO2N. Figure 6a, b, and c show that the effects of anions on spatial distribution of aqueous phase density. The comparative results indicate that Ca^{2+} and Mg^{2+} slow down the process of convective mixing because of the reduction in the dissolved CO_2 , which induces the decrease in the difference of gravity. This finally results in a decrease in CO_2 dissolution rate (See Figure 7). Comparing Base Case 1 to Case 3 (see Figure 6a and d), we find that although the dissolved CO_2 in Case 3 is more than that in Base Case 1, the quantity of total dissolution trapping in Base Case 1 is higher than that in Case 3. This is because the initial density of aqueous in Case 3 is greater than that in Case 1. The increase in the percent of density in Case 3 is smaller than that in Base Case 1, which makes the convective mixing slow.

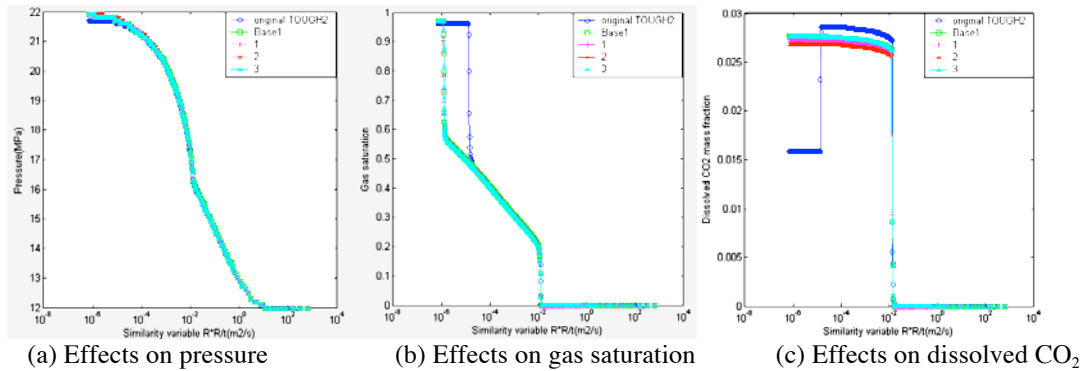


Figure 4. Time evolution for effects of groundwater aqueous components on pressure, gas saturation and dissolved CO_2 ($x=25.25\text{m}$)

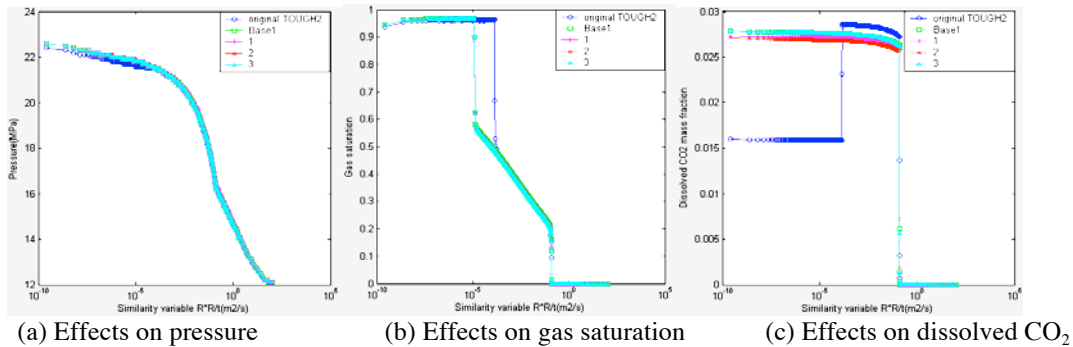


Figure 5. Spatial distribution for effects of groundwater aqueous components on pressure, gas saturation and dissolved CO_2 ($t=27.38\text{years}$)

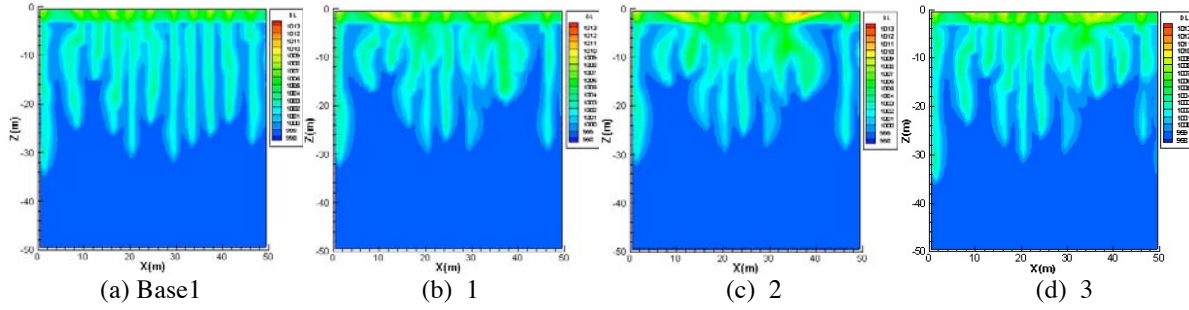


Figure 6. Spatial distribution of aqueous phase density (unit is kg/L) after 150 years

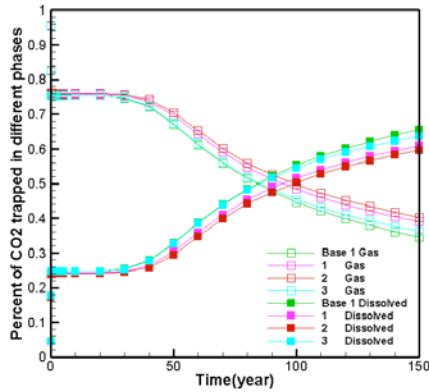


Figure 7. Time evolution of CO₂ trapped in gas and aqueous phases

6. CONCLUDING REMARKS

In comparing the two solubility models (Duan's and original TOUGH2/ECO2N's) using two example problems, we find that:

- (1) The effects of different ions on CO₂ solubility are not the same, and we incorporate Duan's solubility model into TOUGH2/ECO2N as an option to consider the difference.
- (2) An increase in salinity, the equivalent mole fraction of Ca²⁺+Mg²⁺ compared to Na⁺/K⁺, and that of Cl⁻ compared to SO₄²⁻ under the low salinity, results in a decrease in CO₂ solubility. High pressures and low temperatures are helpful for CO₂ solubility.
- (3) According to the two sample problems, the effects of groundwater composition on CO₂ geologic sequestration are mainly demonstrated by the dissolved CO₂. The pressure and gas saturation have no obvious response to differences in groundwater aqueous composition.

Our comparative study and simulation results are specific to the conditions and parameters considered. However, our study has also provided further detail on how groundwater composition affects CGS. Water-rock interaction plays an important role in CO₂ storage, and mineral dissolution could produce more ions affecting CO₂ solubility. This paper does not consider all these processes, making them a possible subject of future work.

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